

*Amal* Cosmetic composition based on associative polyurethanes  
and fatty-chain anionic polymers

The present invention relates to cosmetic  
5 compositions containing a novel system for thickening  
aqueous media based on associative polyurethanes and  
fatty-chain anionic polymers, as well as to their use  
as leave-in haircare gels or styling gels.

The thickening and/or gelation of aqueous  
10 media with polymers has been an important subject of  
cosmetic research for a long time. The production of an  
advantageous thickening effect with a water-soluble  
polymer generally assumes a high molar mass and a large  
hydrodynamic volume. The gelation of an aqueous medium  
15 is thus considered as the result of a three-dimensional  
polymer network obtained by crosslinking linear  
polymers or by copolymerizing bifunctional and  
polyfunctional monomers. However, the use of such  
polymers of very high molar mass poses a certain number  
20 of problems, such as the relatively unpleasant texture  
and the difficulty in spreading the gels obtained.

One advantageous approach consisted in using,  
as thickeners, polymers capable of reversibly  
associating with each other or with other molecules or  
25 particles. This physical association gives rise to  
thixotropic or rheofluidizing macromolecular systems,

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i.e. systems whose viscosity depends on the shear forces to which they are subjected.

Such polymers capable of reversibly associating with each other or with other molecules are known as "associative polymers". The interaction forces in play can be of very different nature, for example of electrostatic nature, of hydrogen-bond type or hydrophobic interactions.

One specific case of associative polymers is amphiphilic polymers, i.e. polymers comprising one or more hydrophilic portions which make them soluble in water, and one or more hydrophobic zones via which the polymers interact and assemble with each other or with other molecules.

It is known practice to prepare hair compositions in gel form using, as thickening system, such associative amphiphilic polymers, in conjunction with surfactants. It is thought that the advantageous rheological properties of the gels thus obtained are due to the formation of mixed micelles containing the surfactants and the hydrophobic portions of the amphiphilic polymers, these micelles constituting a multitude of physical crosslinking points.

However, these compositions based on associative polymers and surfactants do not always have the desired cosmetic properties. Thus, the presence of surfactants, even in small amounts, can adversely modify the cosmetic properties of the said

compositions, such as the properties of application or of feel after drying. Moreover, in particular in the sector of leave-in care gels or styling gels, it is important to be able to distribute the product

5 uniformly over the entire head of hair so as to avoid the overloads and the cosmetic defects resulting therefrom.

European patent application EP-A-0,412,705 describes cosmetic compositions, in particular cosmetic  
10 hair compositions, using, as thickening system, nonionic water-soluble polymers modified by introduction of fatty chains, in combination with one or more natural or synthetic water-soluble polymers.

French patent application FR-A-2,733,910  
15 discloses compositions for styling mousses containing, in combination, at least one anionic polymer and at least one associative polyurethane, at least one of these two polymers having foaming power, so as to improve the properties of the mousses obtained.

20 It has now been discovered that it is possible to obtain a good thickening, or even gelling, effect and advantageous cosmetic properties by combining associative amphiphilic polyurethanes with anionic polymers comprising at least one fatty-chain  
25 monomer unit.

The gel obtained by combining these two types of polymer has a very creamy texture and is pleasant to apply. The final feel on dried hair is more pleasant

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and less laden. The gel moreover has excellent styling power.

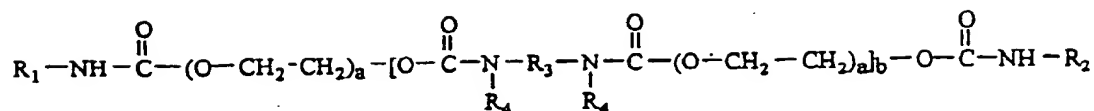
One subject of the present invention is thus a cosmetic composition comprising at least one nonionic  
5 associative polyurethane in combination with at least one anionic polymer comprising at least one fatty-chain monomer unit.

Another subject of the present invention is the use of the combination of at least one nonionic  
10 associative polyurethane and at least one anionic polymer comprising at least one fatty-chain monomer unit, as a thickening system for cosmetic compositions.

A third subject of the invention is a cosmetic process for treating the hair using a cosmetic  
15 composition obtained by combining at least one nonionic associative polyurethane and at least one anionic polymer comprising at least one fatty-chain monomer unit.

Other subjects will become apparent on  
20 reading the description and the examples which follow.

The cosmetic compositions in accordance with the invention are essentially characterized in that they contain, in a cosmetically acceptable medium,  
(A) at least one amphiphilic nonionic associative  
25 polyurethane corresponding to the general formula



(I)

in which

one of the residues  $R_1$  and  $R_2$  represents a higher  $C_8$ - $C_{18}$  alkyl group and the other represents a lower  $C_1$ - $C_6$  alkyl group,

$R_3$  represents a  $C_4$ - $C_{36}$ , preferably  $C_6$ - $C_{10}$ , hydrocarbon-based radical,

$R_4$  represents a hydrogen atom or a  $C_1$ - $C_6$  alkyl radical, preferably a hydrogen atom,

$a$  ranges, independently, from 90 to 600, and  $b$  is from 1 to 4, and

(B) at least one anionic polymer comprising at least one fatty-chain monomer unit.

According to the invention, the expression "lower  $C_1$ - $C_6$  alkyl group" means an alkyl group containing a linear or branched chain comprising from 1 to 6 carbon atoms, such as methyl, ethyl, n-propyl, n-butyl, n-pentyl and n-hexyl radicals, as well as the corresponding branched isomers.

In accordance with the invention, the higher  $C_8$ - $C_{18}$  alkyl groups denote alkyl groups containing a linear or branched chain comprising from 8 to 18 carbon atoms, such as octyl, nonyl, decyl, undecyl, dodecyl,

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tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl radicals.

In one preferred embodiment, one of the alkyl radicals  $R_1$  and  $R_2$  in an  $\alpha$ - $\omega$  position represents an octadecyl group and the other represents a methyl group. The associative polyurethanes used in the compositions of the present invention are used in the form of an aqueous suspension or solution optionally containing a certain amount of soluble starch. This starch can be any starch extracted from natural sources, such as wheat starch, corn starch, rice starch, potato starch, etc., and which has been chemically, enzymatically or microbiologically modified so as to be soluble in water.

A preferred polymer is sold by the company Rohm & Haas under the name Acrysol 46. It is a polyurethane obtained by coupling hexamethylene diisocyanate and polyethylene glycol, and bearing at its ends, respectively, on average one methyl residue and one octadecyl residue. This polymer is in the form of an aqueous solution containing 15% by weight of active polyurethane material and also containing 3-5% of an enzymatically modified starch matrix.

The fatty-chain anionic polymers of the present invention constituting the component (B) are, in particular, polymers comprising units derived from carboxylic acids, from phosphonic acids or from

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sulphonic acids, and at least one unit bearing a fatty chain.

The anionic groups are chosen, for example, from groups derived from carboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid, sulphonic acids, such as vinylsulphonic acid or styrenesulphonic acid, or phosphonic acids, such as vinylphosphonic acid or styrenephosphonic acid.

10           The fatty-chain anionic polymers of the present invention can also contain one or more nonionic units that are well known in the art, for example units derived from vinyl, olefinic, styrene, acrylic or methacrylic monomers. Examples of such monomers which  
15 may be mentioned are ethylene, propylene, styrene, vinyl acetate and alkyl acrylates and methacrylates.

The fatty chains are linear or branched  $C_8$ - $C_{22}$  alkyl groups. They can be derived from monomers such as  $C_8$ - $C_{22}$  alkyl acrylates or methacrylates or vinyl esters  
20 of higher  $C_8$ - $C_{22}$  fatty acids.

The fatty-chain anionic polymers of the present invention can be prepared by copolymerizing anionic monomers and monomers comprising at least one fatty chain, and optionally nonionic monomers. It may  
25 also be envisaged to prepare them by introducing the anionic groups and the fatty chains by grafting or chemical modification of natural or synthetic polymers.

Examples of preferred anionic polymers of the present invention which may be mentioned are terpolymers of acrylic acid, vinylpyrrolidone and C<sub>8</sub>-C<sub>18</sub> alkyl methacrylate, for example lauryl methacrylate, 5 such as the product sold under the name Acrylidone LM by the company ISP; terpolymers of vinyl acetate, monoisobutyl maleate and a C<sub>10</sub>-C<sub>20</sub> vinyl alkanoate, for example vinyl neodecanoate, such as the product sold under the name Meypro-Fix 509 by the company Rhône 10 Poulenc Surfactants; and the terpolymers of vinyl acetate, of crotonic acid and of a C<sub>10</sub>-C<sub>20</sub> vinyl alkanoate, for example vinyl neodecanoate, such as the product sold under the name National 28-2930 by the company National Starch.

15 According to the invention, the associative polyurethanes and the fatty-chain polymers are used in amounts which are sufficient to obtain satisfactory thickening or gelation of the aqueous medium.

An amount of associative polyurethanes of 20 between 0.1 and 10% by weight, and preferably between 0.5 and 5% by weight, expressed as active material and relative to the total weight of the composition, is recommended in particular.

In the compositions of the present invention, 25 the anionic polymers comprising at least one fatty chain are present in a proportion of from 0.01 to 10% by weight, preferably in a proportion of from 0.1 to 5%



by weight, of active material relative to the total weight of the composition.

In the present invention, the ratio of the said nonionic associative polyurethane (A), of formula (I) to the said anionic polymer comprising at least one fatty-chain monomer unit (B) is preferably within the range from 90/10 to 10/90.

The cosmetically acceptable medium preferably consists of water and can also contain cosmetically acceptable solvents, for example lower monoalcohols such as ethanol or isopropanol, glycols such as diethylene glycol, glycol ethers such as ethylene glycol alkyl ether or diethylene glycol alkyl ether, or alternatively fatty acid esters, all these solvents being used alone or in the form of a mixture.

The haircare or styling gels can also contain one or more additives commonly used in such hair compositions. Examples which may be mentioned are fragrances, dyes, preserving agents, sunscreens, vitamins, pH regulators, etc. It is clearly understood that the choice of these compounds should take into account any interactions with the thickening system. A person skilled in the art will take care to ensure that the addition of these additives will not have an unfavourable effect on the advantageous properties of the compositions obtained by virtue of the present invention.

A preferred cosmetic process for treating the hair, according to the invention, consists in applying and uniformly distributing the compositions described above on the hair and in drying the hair thus treated  
5 without rinsing it.

The examples which follow are intended to illustrate the invention without thereby being limiting in nature.

10 **Example 1**

The aqueous compositions below are prepared:

Acrysol 46, a product sold by the company Rohm & Haas, a polyurethane obtained by coupling  
15 hexamethylene diisocyanate and polyethylene glycol, and bearing at its ends, respectively, on average one methyl residue and one octadecyl residue. The resin National 28-2930 sold by the company National Starch is an anionic terpolymer obtained by copolymerizing vinyl  
20 acetate, crotonic acid and vinyl neodecanoate.

This example shows that the combination of the preferred associative polyurethane of the present invention (Acrysol 46) and a fatty-chain anionic polymer (National 28-2930) makes it possible to obtain  
25 a gel which has excellent cosmetic properties. Hair treated with this composition A is easy to disentangle and feels smooth and supple.

It is noted that Acrysol 46 alone  
(composition B) has no appreciable thickening effect,  
let alone a gelling effect.

Composition A also has the advantage of being  
5 creamy and non-greasy and of not being sticky.

### Example 2

A care gel having the composition below was  
10 prepared:

Acrysol 46	2% active material
Acrylidone LM*	1% active material
2-Amino-2-methyl-1-propanol	qs neutralization
Fragrance, dye, preserving	
15 agent and demineralized water	qs 100 g

\*Acrylidone LM is an anionic terpolymer obtained by  
copolymerizing acrylic acid, vinylpyrrolidone and  
lauryl methacrylate (68/23/9%), sold by the company  
I.S.P.

20

### Example 3

A care gel having the composition below was  
prepared:

25 Acrysol 46	2% active material
Acrylidone LM	2% active material
2-Amino-2-methyl-1-propanol	qs neutralization
Fragrance, dye, preserving	

agent and demineralized water                    qs 100 g

### Example 4

5                   A care gel having the composition below was  
prepared:

Acrysol 46 3% active material

Meypro-Fix 509\* 2% active material

2-Amino-2-methyl-1-propanol                      qs neutralization

10	Fragrance, dye, preserving	
	agent and demineralized water	qs 100 g

Maypro-Fix 509 is an anionic terpolymer of vinyl acetate, monoisobutyl maleate and vinyl neodecanoate, sold by the company Rhône-Poulenc Surfactants.

It is clearly understood that the description hereinabove has been given for purely illustrative purposes and without any limitation being implied, and that variants or modifications may be made in the context of the present invention.